

DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Pilot-Scale Biochemical and Hydrothermal Integrated Biorefinery (IBR) for Cost-Effective Production of Fuels and Value Added Products

Date: March 26, 2021

Technology Area Session: Systems Development and Integration

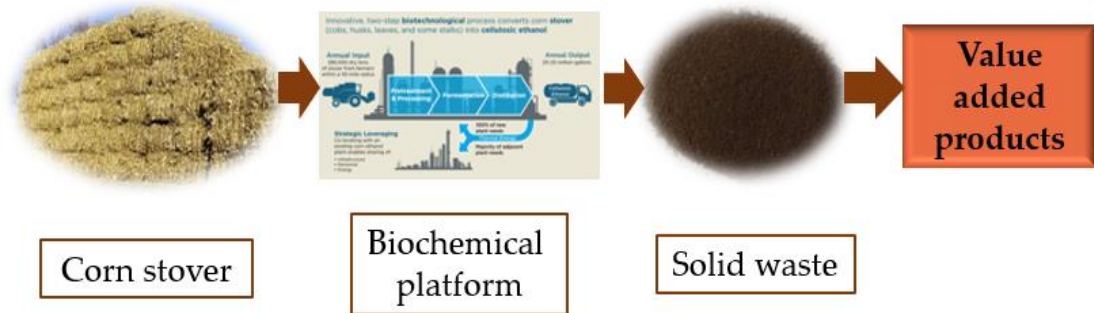
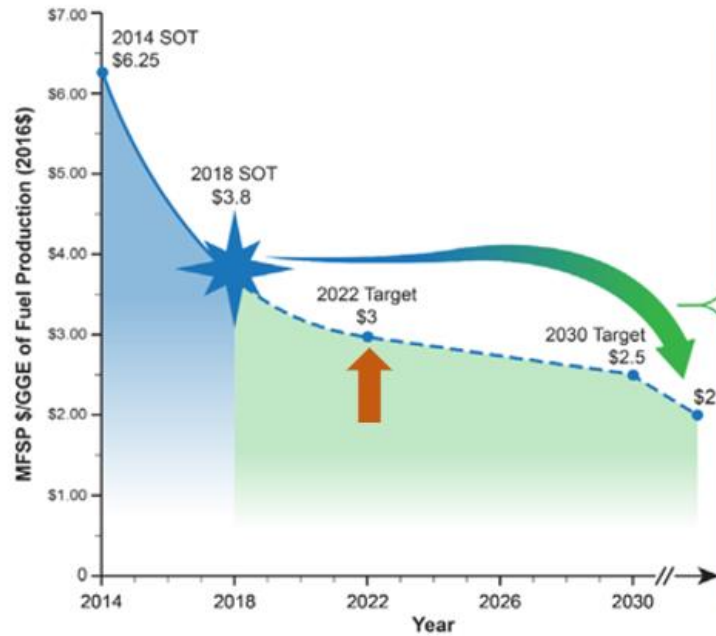
Principal Investigator: Rajesh Shende

Organization: South Dakota School of Mines & Technology

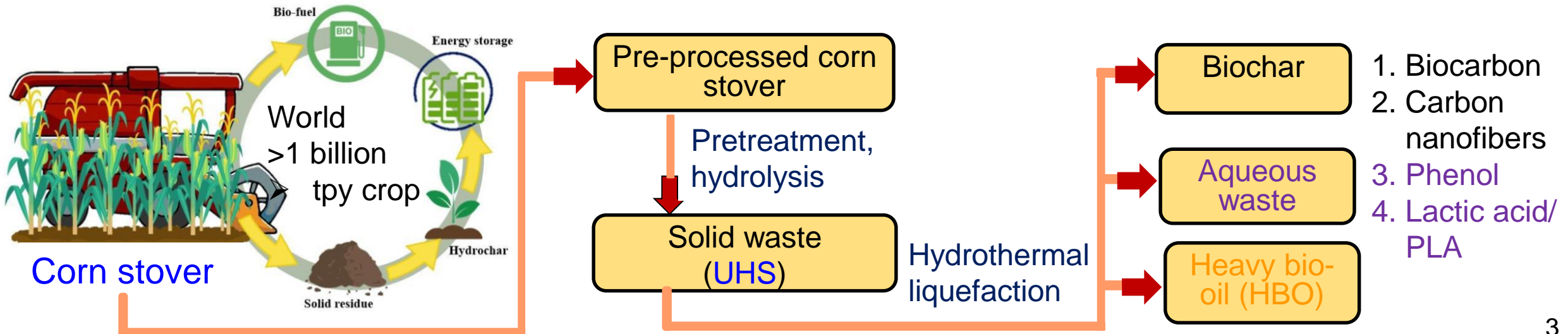
Goal Statement

- ❖ Demonstrate production of high value products from waste streams (as defined below) generated during conventional biochemical processing at a pilot scale level with 1 tpd throughput.
 - Aqueous waste stream (I) from alkaline pretreatment of corn stover
 - Solid waste residue (I), unhydrolyzed solids (UHS)
 - Aqueous waste stream (II) from hydrothermal processing
 - Biochar waste (II)
- ❖ **Outcomes:** i) Four products from solid waste and aqueous waste, which include biocarbon, carbon nanofibers, lactic acid/PLA and phenols and ii) inclusion of revenues derived from these products into TEA and LCA demonstrating BETO's 2022 cost target of \$3/gge with >50% reduction in GHGs emission.

Project Overview

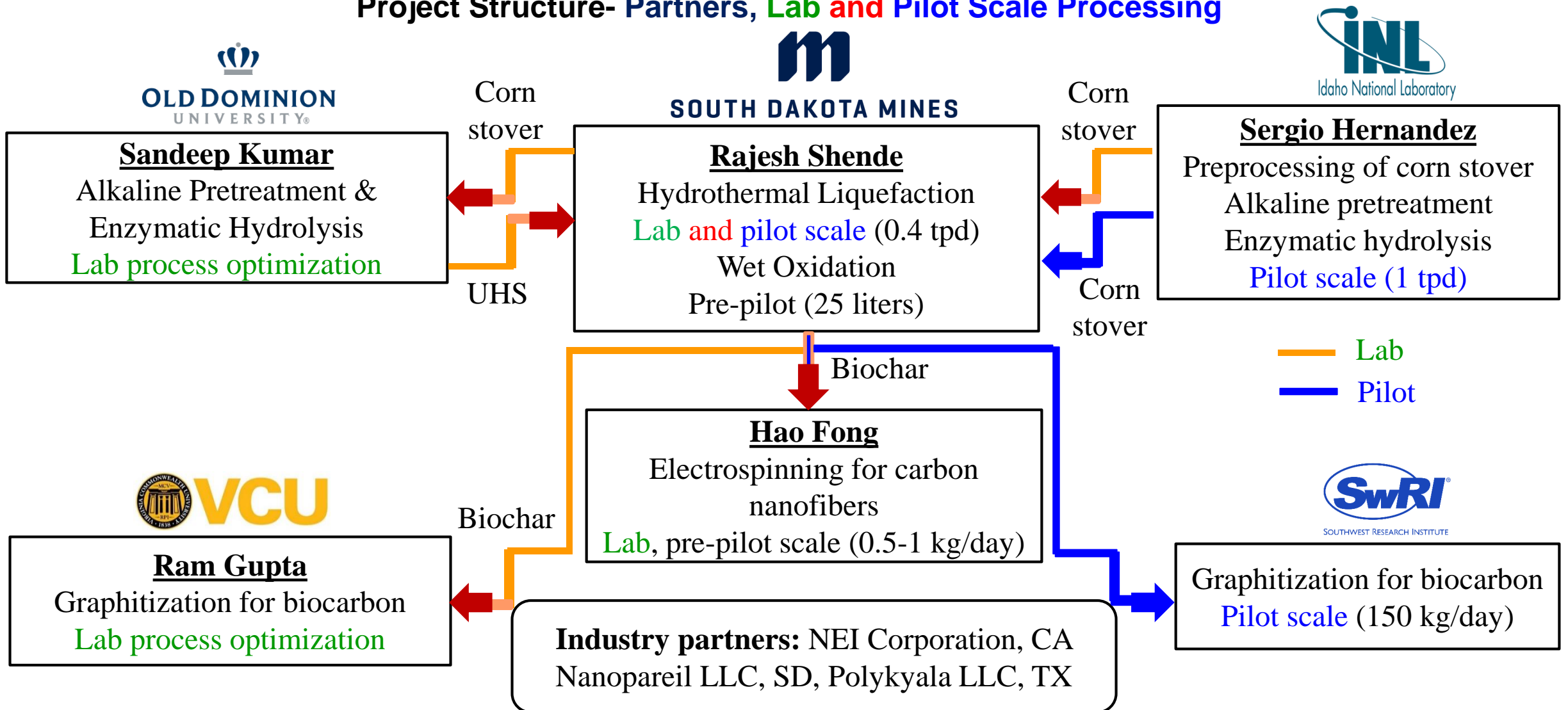


<https://www.energy.gov/sites/prod/files/2020/07/f76/beto-integrated-strategies-to-enable-low-cost-biofuels-july-2020.pdf>; Ruan et al., *Integrated Processing Technologies for Food and Agricultural By-Products*, Academic Press (2019); 2016 Billion-Ton Report, USDOE.

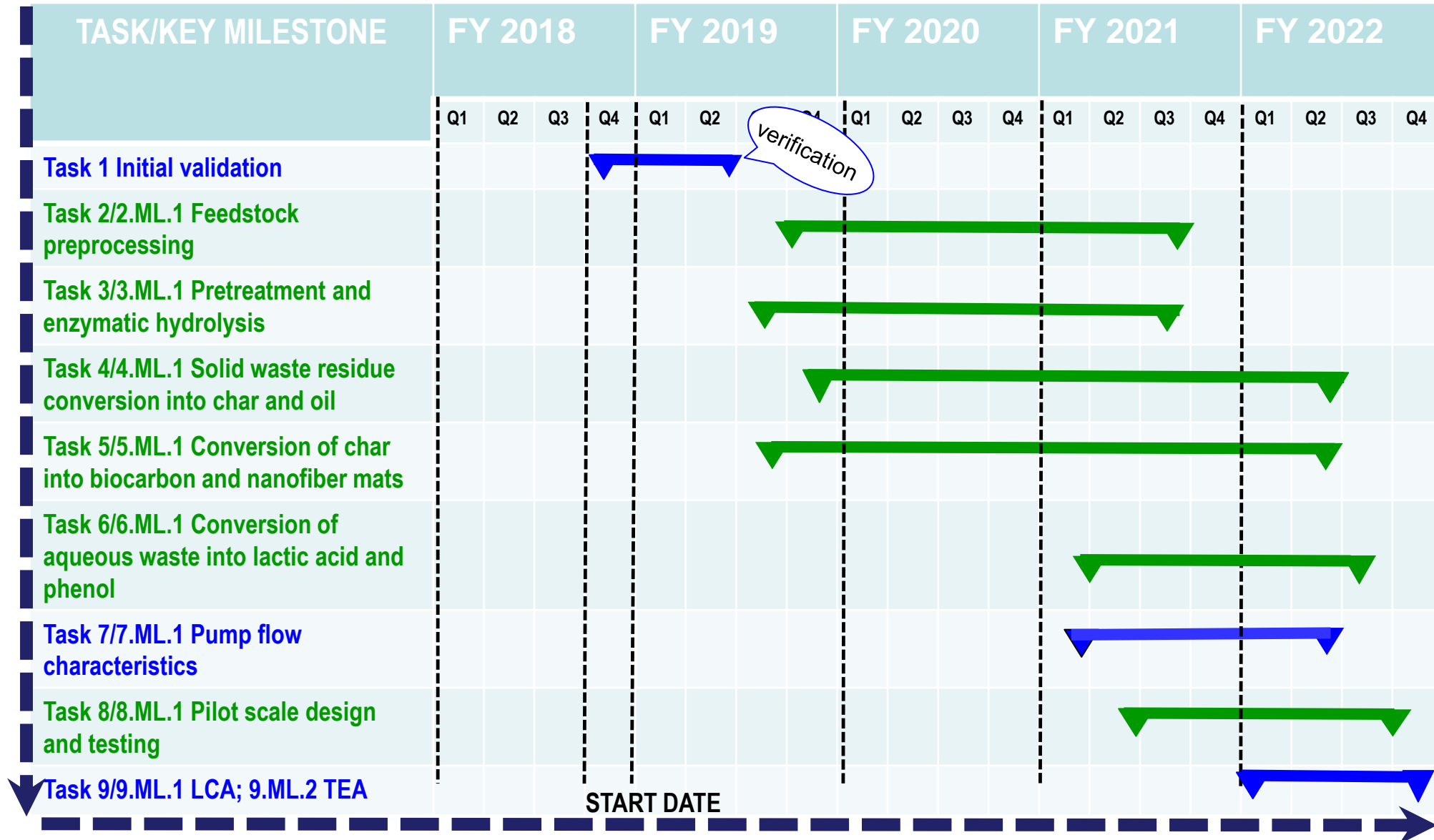


1- Project Management

Project Structure- Partners, Lab and Pilot Scale Processing



Project Timeline



NOTE: GREEN lines and text indicate Active Status; BLUE lines and text indicate Inactive Status

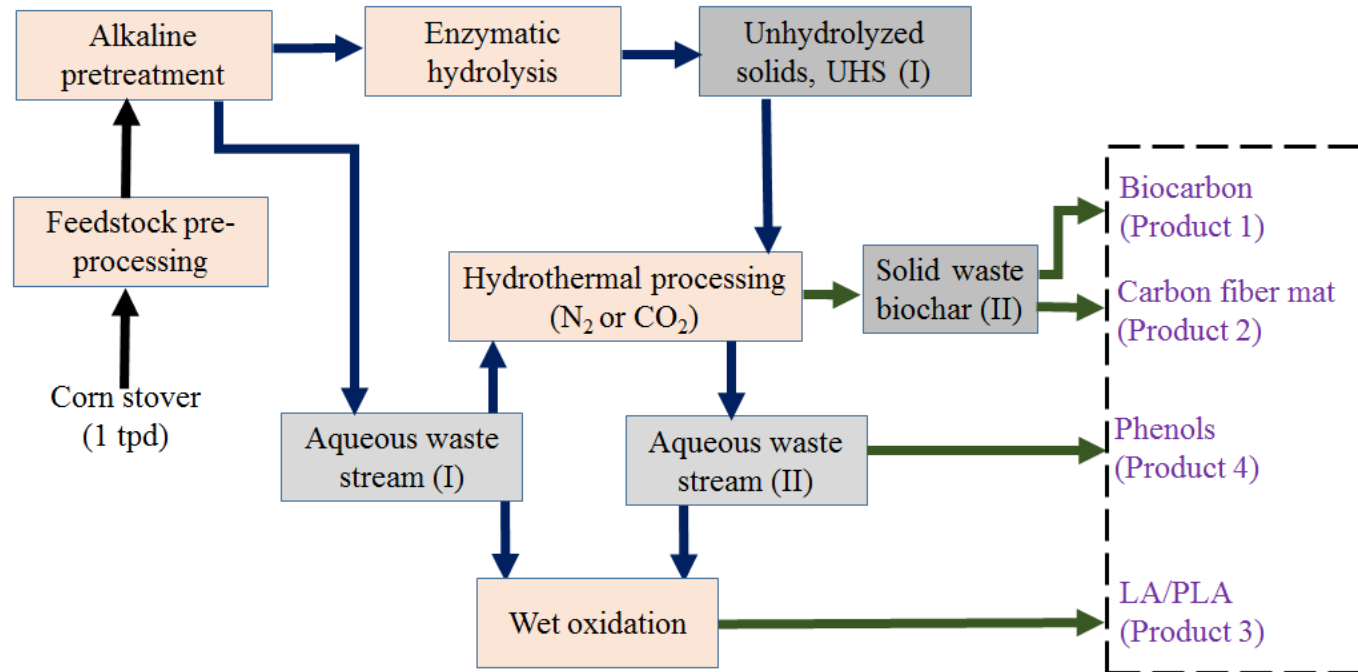
Project Risks & Mitigation

SI No.	Project Risk	Mitigation by Management Approach
1	Optimization of processing conditions to be used for pilot scale trials (technical)	Use of DOE software for statistical analysis and response surface methodologies
2	Selectivity of graphitization conditions for obtaining battery grade carbon (technical)	Using optimal conditions identified by process simulation
3	Residue issues on nanofiber formation (technical)	Increase the biochar loading, and exploring nanofiber sponge morphology
5	Transportation of UHS and aqueous waste to other locations, system integration (management)	Identifying contractors, addressing scheduling
6	Procurement or configure pilot scale equipment for 1 tpd corn stover processing (management)	Identifying vendors, configuring pilot plants, delivery of main parts, addressing delays due to COVID, planning and scheduling

2 - Approach

BETO Focus Area: Enabling biofuels by developing technologies for high value products from biochemical waste processing

Technical

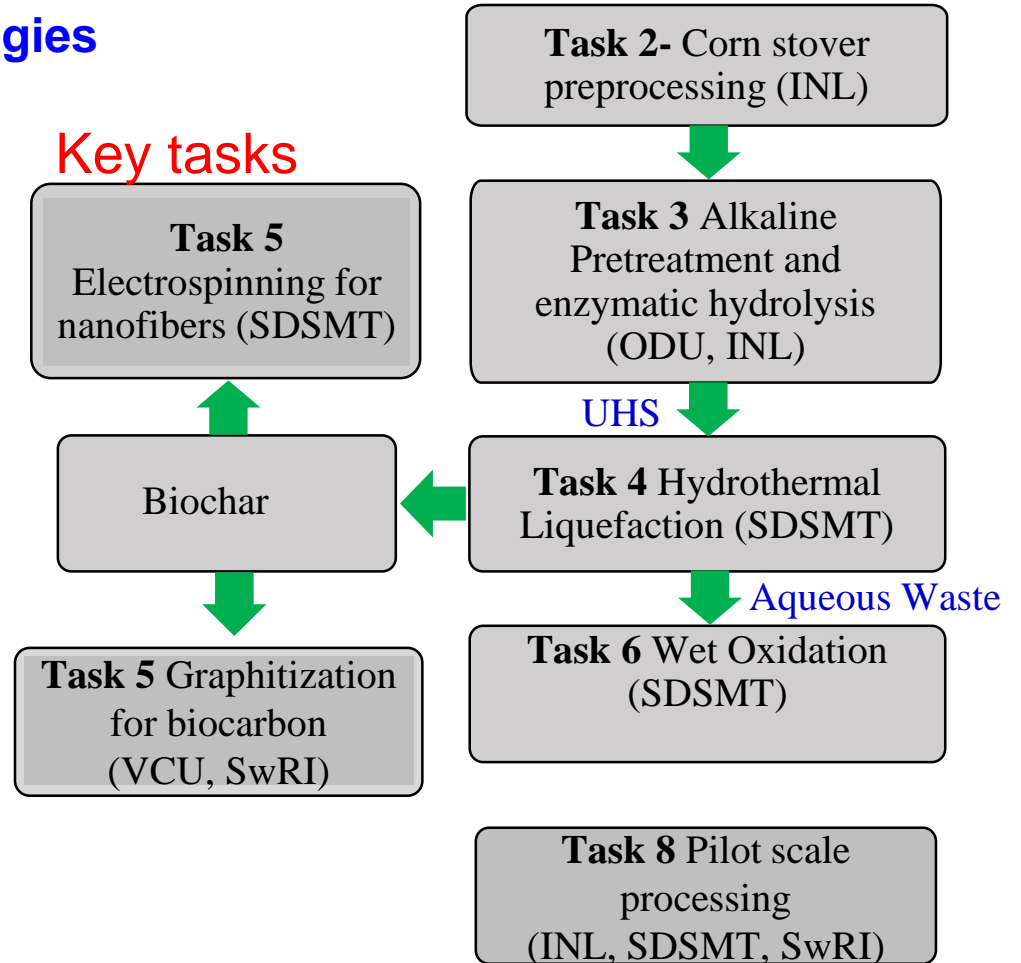


- Lab scale**
- Optimization
 - Mass/energy balance
 - Product yield and quality

- Pilot scale**
- 1 tpd throughput
 - Mass/energy balances
 - Products yield and quality

- TEA/LCA**
- Product cost estimates
 - Processing costs
 - System boundary variations

Key tasks



Tungal et al., *Applied Energy* (2014); Nan et al., *Materials Letters* (2017); Kumar et al., *Biomass Conversion and Biorefinery* (2016); Thakkar et al., *Fuel Processing Tech.* (2021); Shell et al., *Bioresource Tech. Reports* (2021).

Key Milestones, Metrics, Current Status

Key Milestones	Metrics (Expected Yield/Quality)	Current Status
Preprocessing- Milling (2ML.1)	Milled corn stover with ash content <6 wt% and >8 wt%, particle 0.1 mm – 3 mm Preprocessing 5-10 ton corn stover, 300 kg batch for lab processing (pilot)	Pilot scale (INL)- completed (met expectations)
Alkaline Pretreatment and enzymatic hydrolysis (3ML.1)	UHS (K_2CO_3 <0.9 wt.% in water <190 °C, NREL LAP, pH 4.8, <72 h) 1 tpd throughput (pilot)	Lab scale (ODU) – completed (met expectations) Pilot scale (INL) – plant being configured
Hydrothermal liquefaction (HTL) (4.ML.1) Wet oxidation (WO) (6.ML.1)	HTL: Lactic acid 10 wt.%, char >20 wt.% up to 35 wt.% and bio-oil 20 wt.% 0.4 tpd UHS (pilot) WO: 10-22 wt% lactic acid	Lab scale (SDSMT) – completed (met expectations) Pilot scale (SDSMT) – planning
Graphitization of biochar (5.ML.1)	Biocarbon, 55% conversion of biochar, 200 F/g specific capacitance, 150 kg/day (pilot)	Lab scale (VCU) – completed (met expectations) Pilot scale (SwRI) – planning
Electrospinning of biochar into nanofibers (5.ML.1)	Carbon nanofibers (>50 m ² /g), > 40 wt% biochar loading, 0.5 – 1 kg/day (pre-pilot)	Lab scale (SDSMT) – completed (met expectations) Pilot scale (SDSMT) – planning

Potential Challenges, Key Success Factors

Potential Challenges

- ❖ Yield and quality of value-added products (biocarbon, carbon nanofibers, lactic acid and phenol) at a pilot scale level although we have successfully demonstrated both at the laboratory scale (*technical*)
- ❖ Configuration of some pilot plant equipment for efficiency (*technical*)
- ❖ Integrate processing at different locations (scheduling, transport of UHS and aqueous waste) (*Management*)

Key success factors

- ❖ % agreement between lab and pilot scale trials (yield and quality)
- ❖ Quality assessment of biocarbon and carbon nanofibers by our industry partners
- ❖ In-depth estimation of revenue stream from the value-added products to meet BETO's goal of \$3/gge
- ❖ Life cycle assessment >50% reduction in GHGs

3 – Impact (DOE/BETO)

- ❖ Directly impacting BETO's Mission of developing cost-effective technologies for bio-based products from waste streams.
- ❖ Integrated technologies developed here will generate additional revenue stream from the value-added products and help meeting BETO's 2022 target of \$3/gge.
- ❖ Expected positive impact on the GHG emission, reduction by > 50%.
- ❖ Impacting readily available market with increasing demand for the high value products (in 2020) - biocarbon (\$1.67 billion), carbon nanofibers (\$21.2 million), phenol (\$23.17 billion), lactic acid (\$1.1 billion)

3 – Impact (Partnerships and SD)

- ❖ Positively impacted collaboration among 3 universities, INL, and SwRI with future collaborations with NREL, PNNL and industries.
- ❖ Technology transfer to industries/commercialization- NEI corporation, Nanopareil LLC, Polykyala LLC and EIR at SDSMT ((<https://www.sdsmt.edu/Research/Economic-Development/Entrepreneur-In-Residence-Program/>)
- ❖ Publications- 5 peer-reviewed, 2 under review and 3 under preparation, and many presentations in national and international conferences.
- ❖ Positively impacting South Dakota with bioprocessing pilot scale facilities initiative.

3 – Impact (Outreach and Education)

- ❖ IBR related educational workshop activities are being planned for the local high school and Native American students (Summer 2021) (<https://www.sdsmt.edu/learn/>).
- ❖ Training undergraduate students at SD Mines (CBE 467) to develop process engineering design for integrated bioprocessing. Learning outcomes from the current research activities will be included in the elective courses (CBE485/CBE485L Renewable and Sustainable Energy lecture/lab courses).
- ❖ Positively impacting GRA and salary support to the graduate students, post-docs, and research associates at collaborating institutions.
- ❖ COVID-19 pandemic situation affected project schedule. Extension is/will be requested to make the project successful.

4 - Progress and Outcomes

Preprocessing: Biomass Feedstock National User Facility

- The BFNUF comprises:
 - A full-scale, fully integrated Process Development Unit (PDU) with modular design with a capacity of 2 ton/hr for herbaceous biomass and 5 dry ton/hr for woody biomass.
 - Single-stage or two-stage hammer mill grinding
 - Various mechanical conveyors with Feedstock metering bin
 - Pelletizing (1 ton/hr and 5 ton/hr)

Preprocessed corn stover and supplied to partners

- INL Chemical Preprocessing System (CPS)
 - Unique pretreatment/preprocessing system
 - Ambient $\leq T \leq \sim 200$ °C, Ambient $\leq P \leq \sim 200$ psig
 - Wide pH (0.5 – 13.5), numerous approved solvents
 - Continuous up to 1 dry ton/day
 - Batch reactors (3×10-L, non-agitated)

Currently being configured to achieve 3.ML.1



Feedstock (corn stover) Characterization

Table 1. Proximate and ultimate for corn stover samples

Feedstock	Proximate Analysis (wt. %)				Ultimate Analysis (wt. %)				
	Moisture	Volatile	Ash	Fixed Carbon	H	C	N	O	S
Low Ash Corn Stover	7.67%	77.18	6.75	16.07	5.69	46.25	0.42	40.51	0.09
High Ash Corn Stover	5.39%	68.55	13.03	18.42	5.16	41.62	0.85	39.26	0.09



Low Ash Corn Stover

High Ash Corn Stover

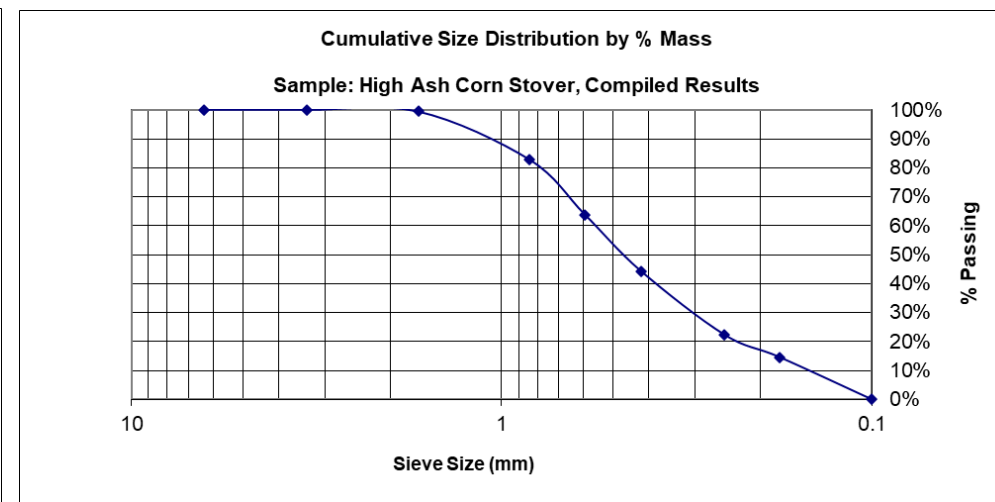
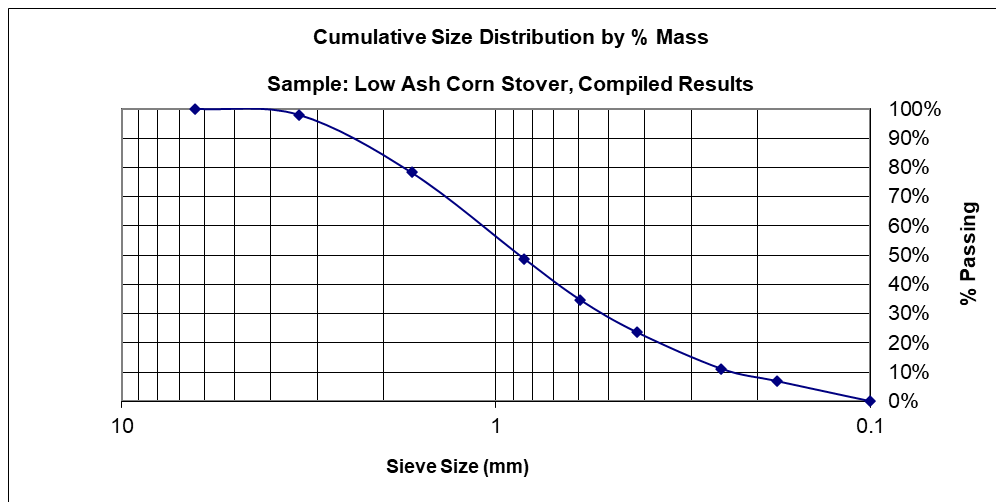
Measurements acquired using ASTM D7582, ASTM D5373, ASTM D4239, and ASTM 5865.

Table 2. Particle size distribution

Feedstock	X_{gm} (mm)	S_{gm} (mm)	d10 (mm)	d50 (mm)	d90 (mm)
Low Ash Corn Stover	1.12	1.15	0.23	0.88	2.68
High Ash Corn Stover	0.60	0.49	0.15	0.47	1.20

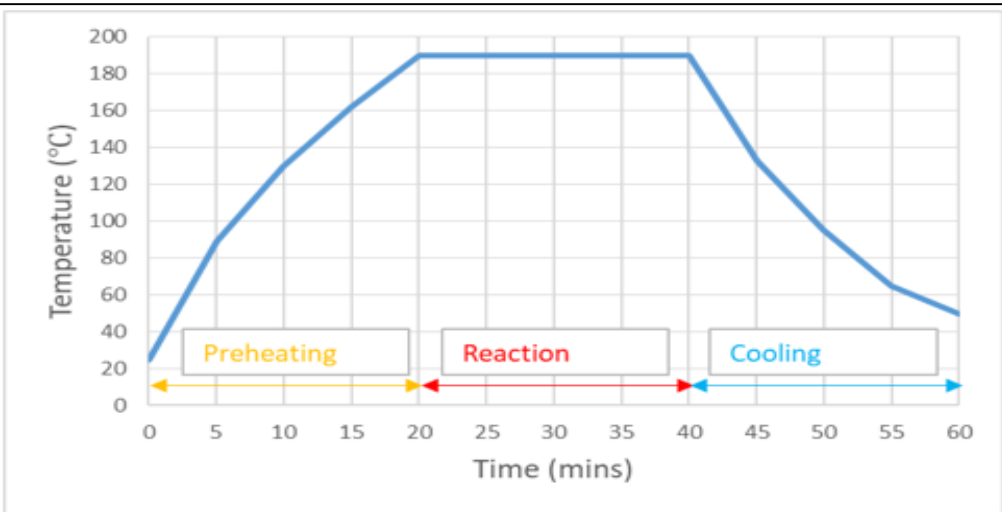
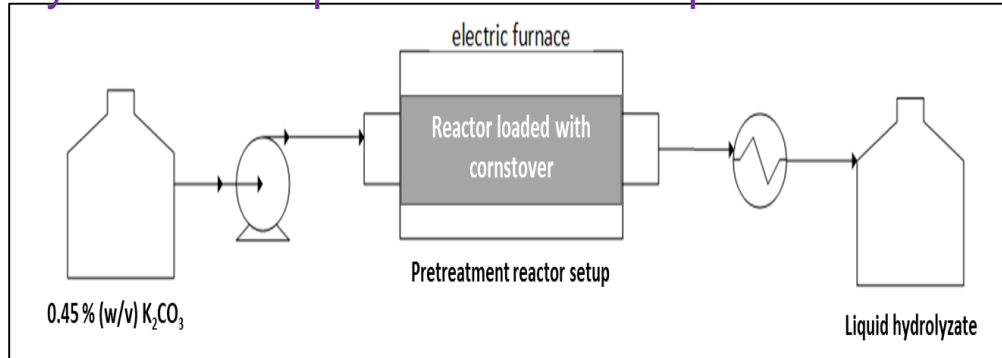
The values determined for Sieve₁₀, Sieve₅₀, and Sieve₉₀ are within the target values (Sieve₁₀ > 0.1 mm and Sieve₉₀ < 3 mm) the project.

Measurements acquired using ASAE S319.3 using a standard Ro-Tap separator (W.S. Tyler model RX-29).



Pretreatment and Enzymatic Hydrolysis

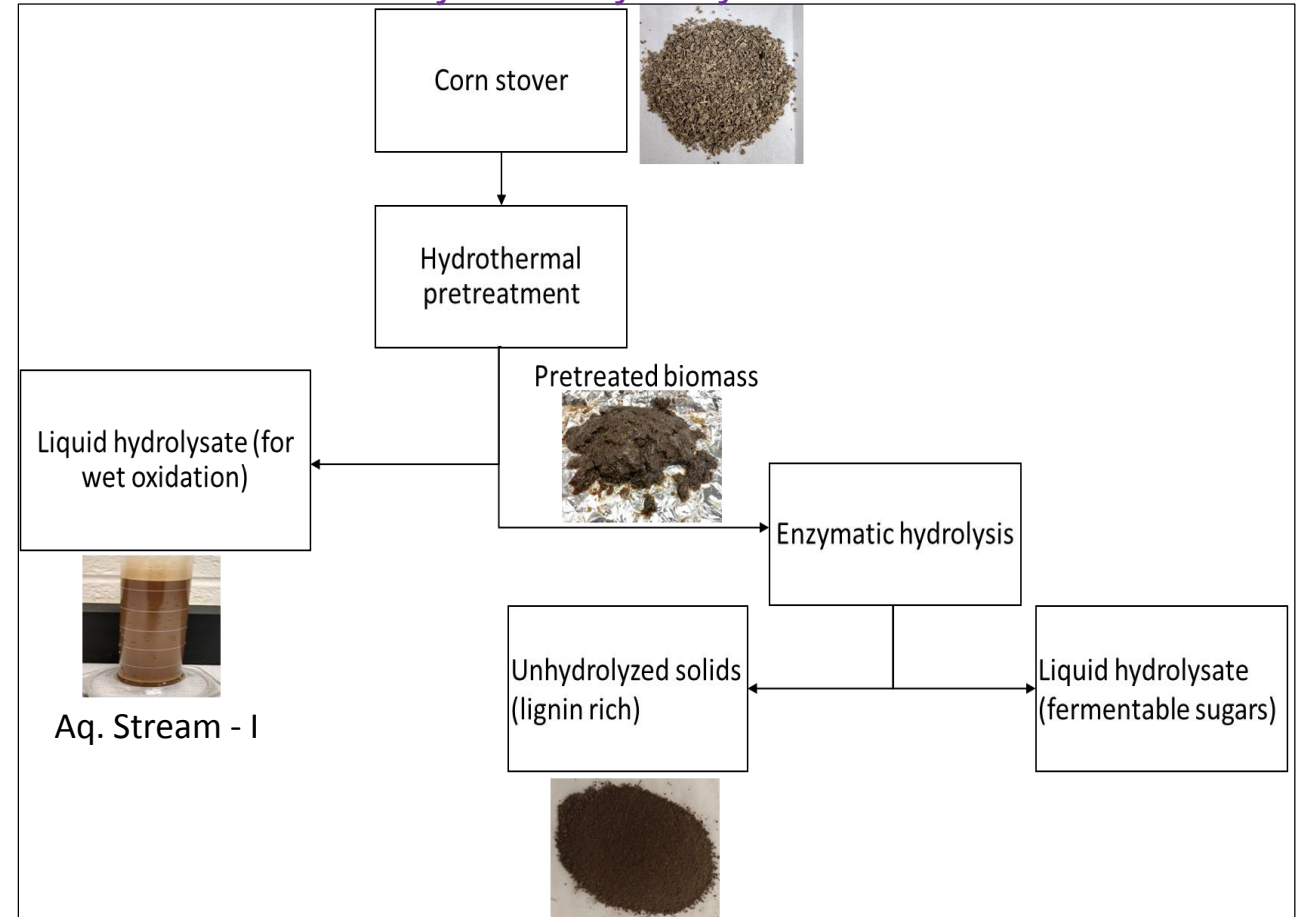
Hydrothermal pretreatment setup



Typical Temperature vs. Time profile for pretreatment of corn stover

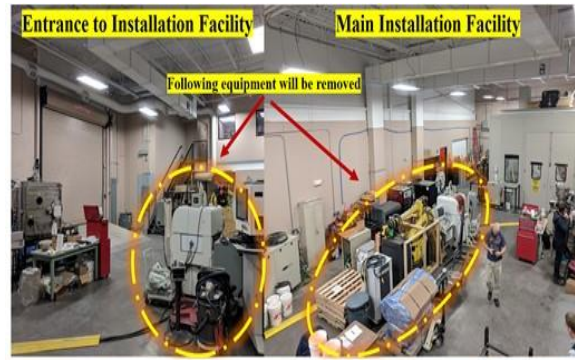
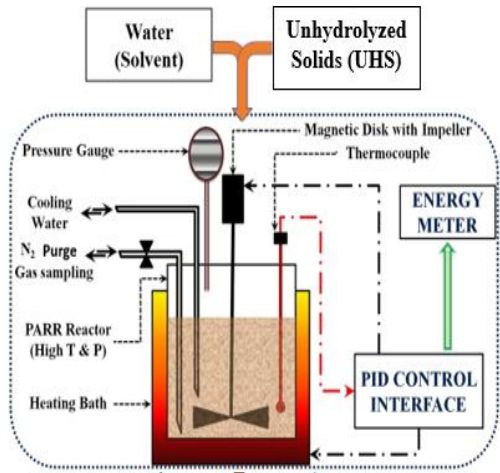
Biomass	Ash (%)	Lignin (%)	Glucan (%)	Xylan (%)	Arabinan (%)	Others (%)
Raw corn stover	6.5	27.0	28.2	21.6	2.5	14.2
Pretreated corn stover	9.4	18.0	62.0	8.7	0.3	1.6

Pretreatment & Enzymatic hydrolysis

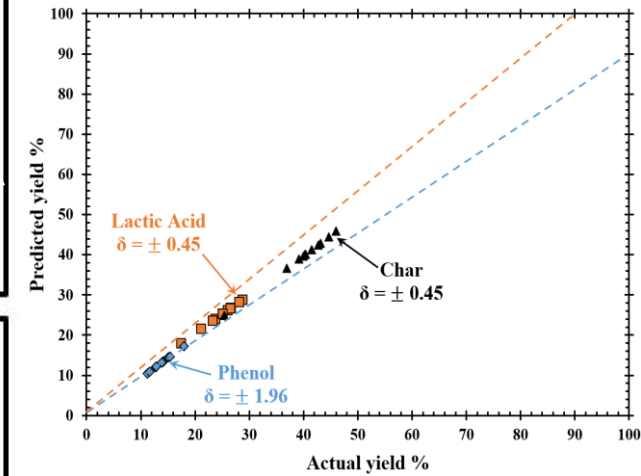
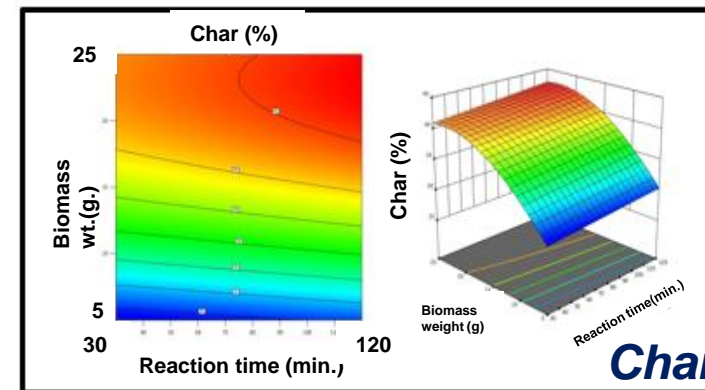
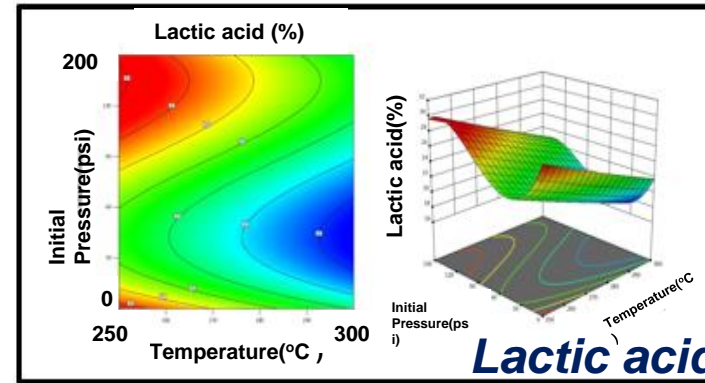
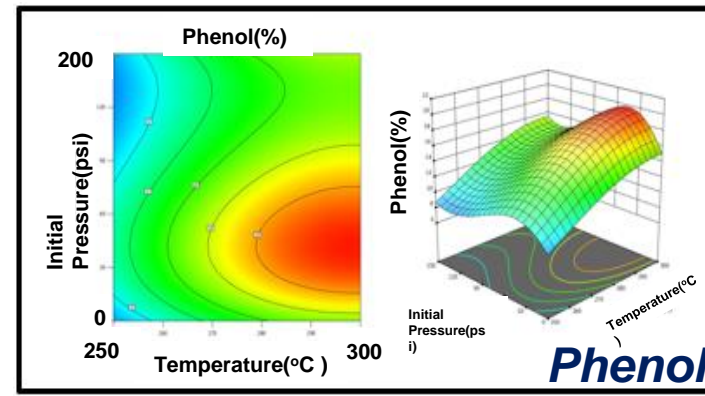


- Total time: 72 hours
- Average glucan conversion: >90 %

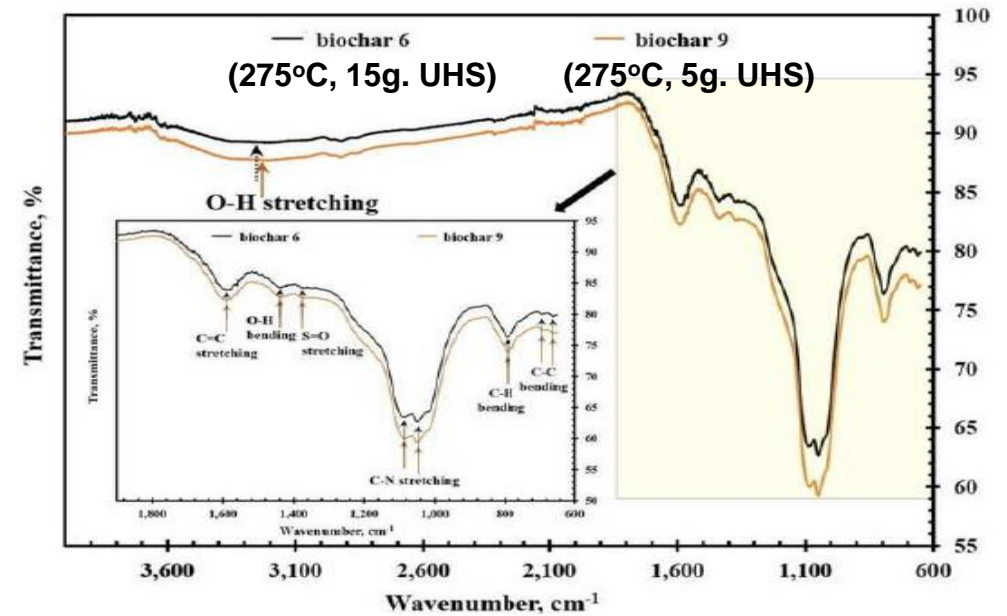
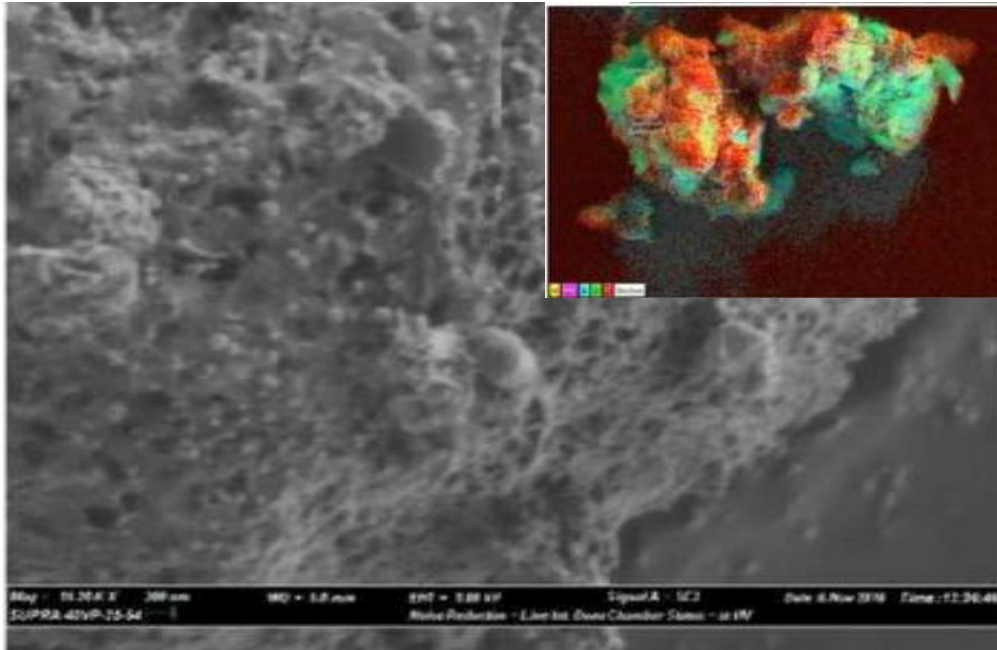
Hydrothermal Liquefaction of UHS



Advantages - Direct wet processing (avoid drying costs), diverse biomass substrates, high value products, bio-oil with high HHV, energy recovery, better char characteristics



Response	Theoretical yield (wt. %)	Experimental yield (wt. %)
Char	42.47	42.67
Lactic acid	27.16	28.12
Phenol	15	11.2



Quality – unique features

Raman microcrystalline size: 4 nm

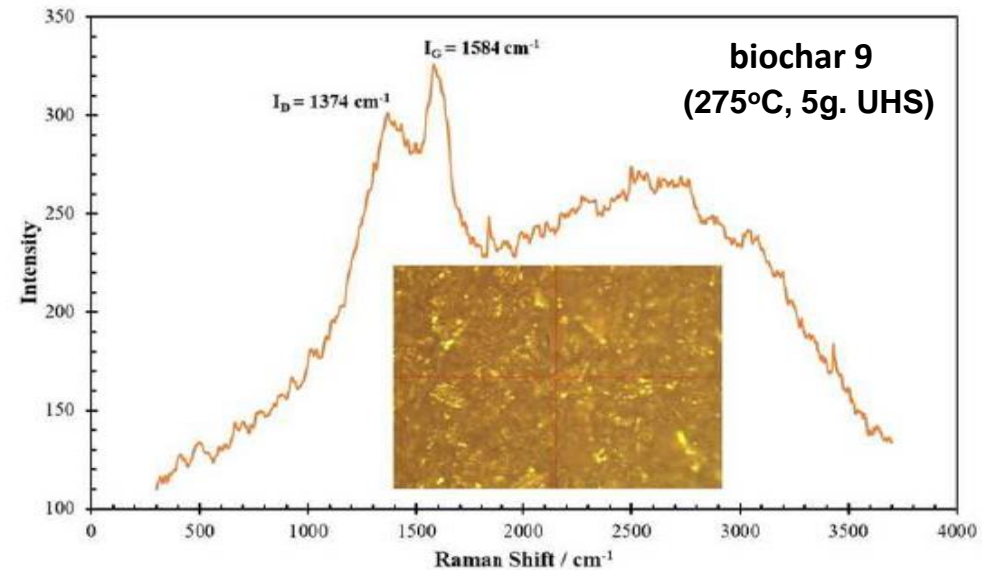
Specific surface area: >50 m²/g - 1300 m²/g

Pore size: 2.8 – 5.5 nm; Pore volume: 0.0184 - 0.899 cm³/g; Specific capacitance (asymmetric Capacitor) - 85% of graphene electrode with (Mn,Ti)-oxide electrode

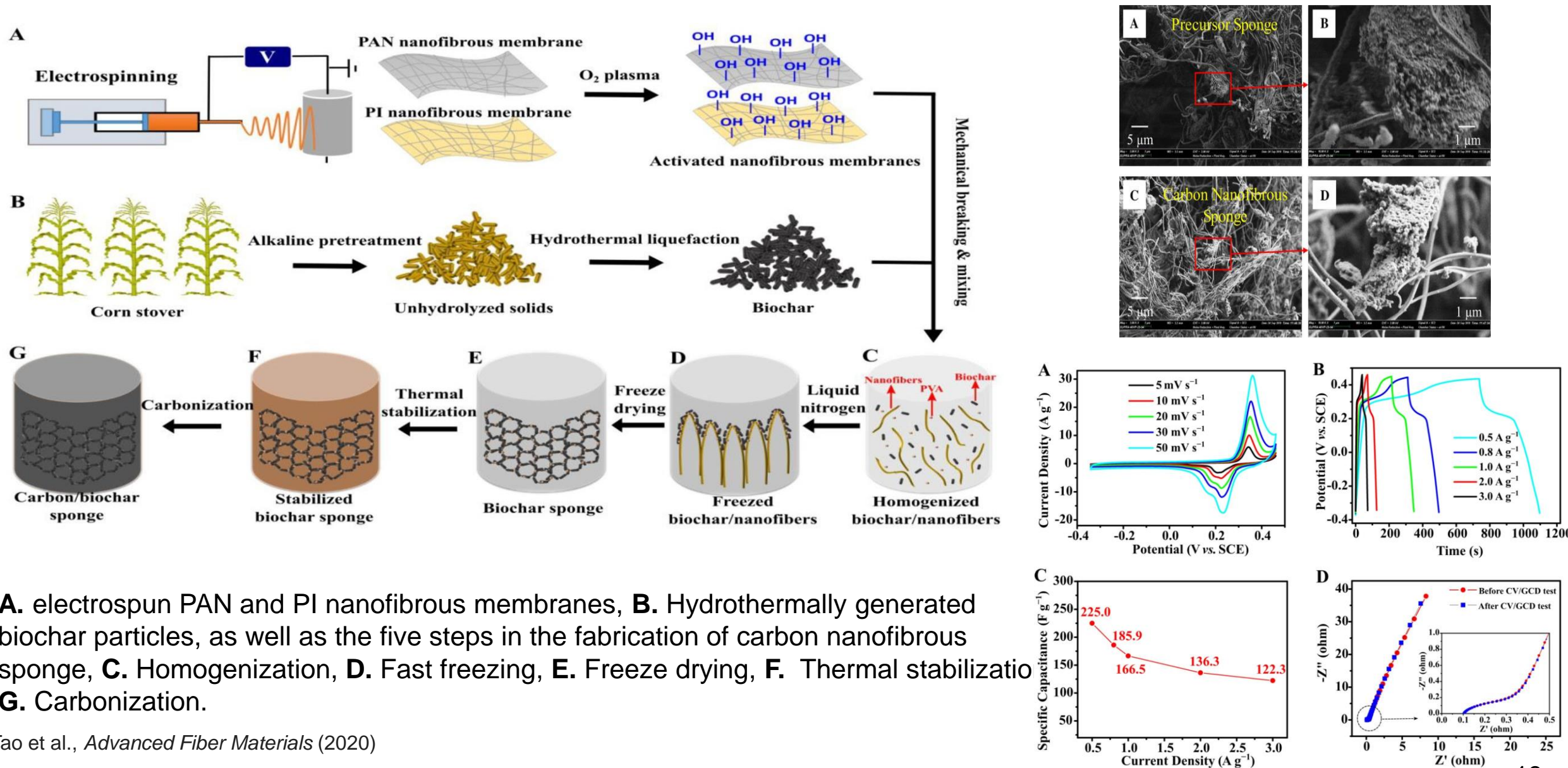
Amar et al., *Renewable Energy*, 2021 (under review).

Amar et al., *Int. Journal of Energy Research* (2020)

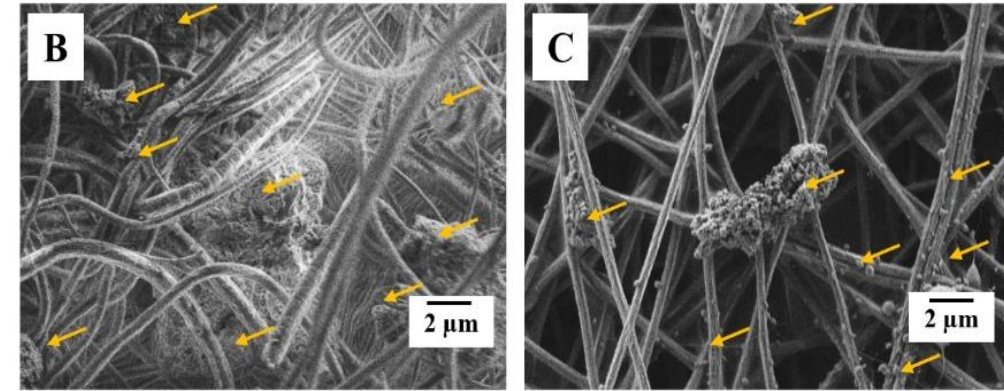
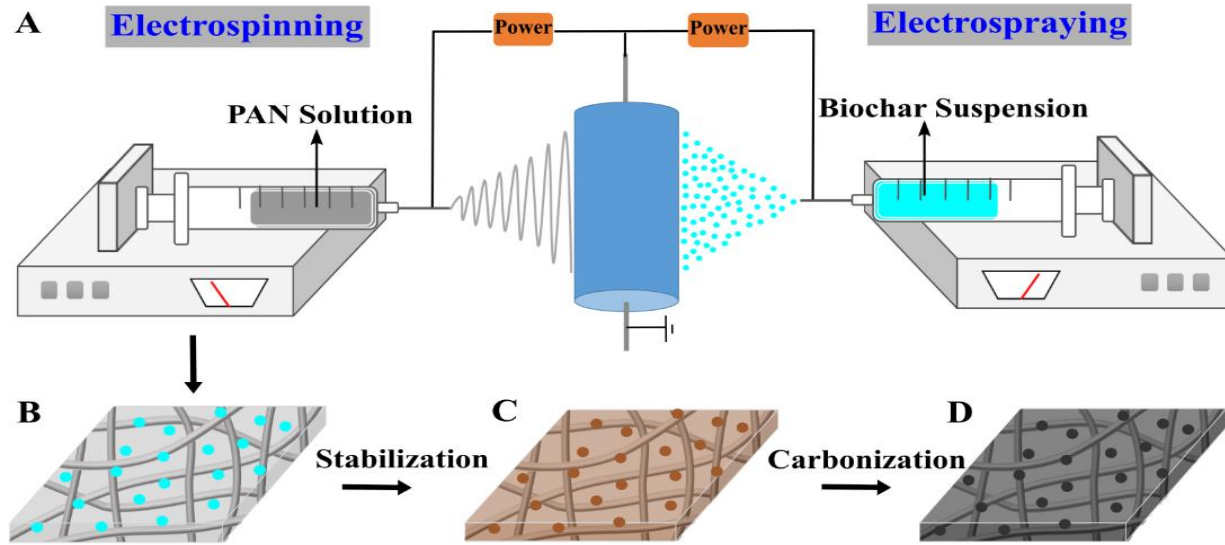
Choudhary et al., *Advanced Materials* (2017).



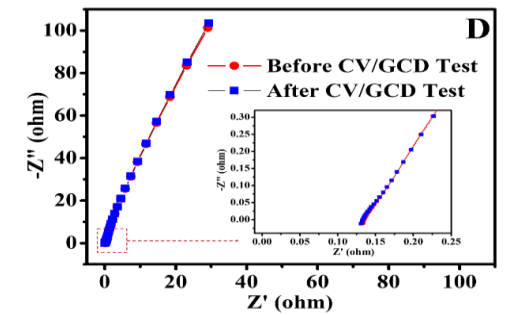
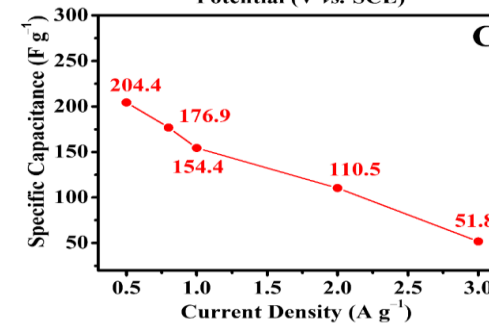
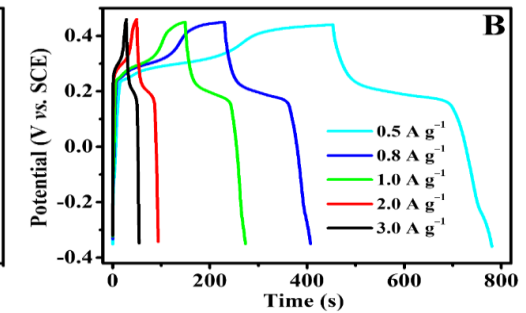
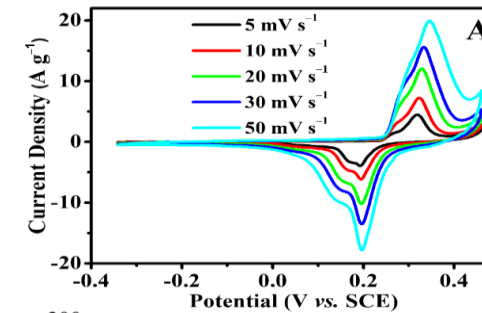
Approach-1 Process for Carbon Nanofibrous Sponge



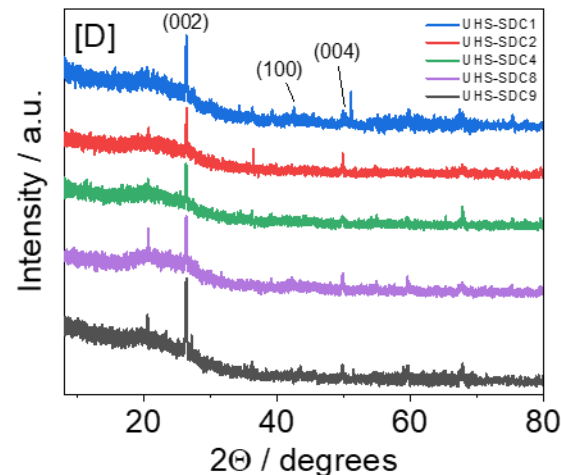
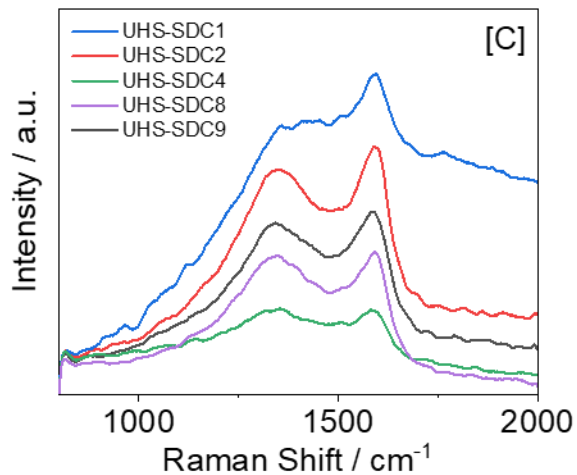
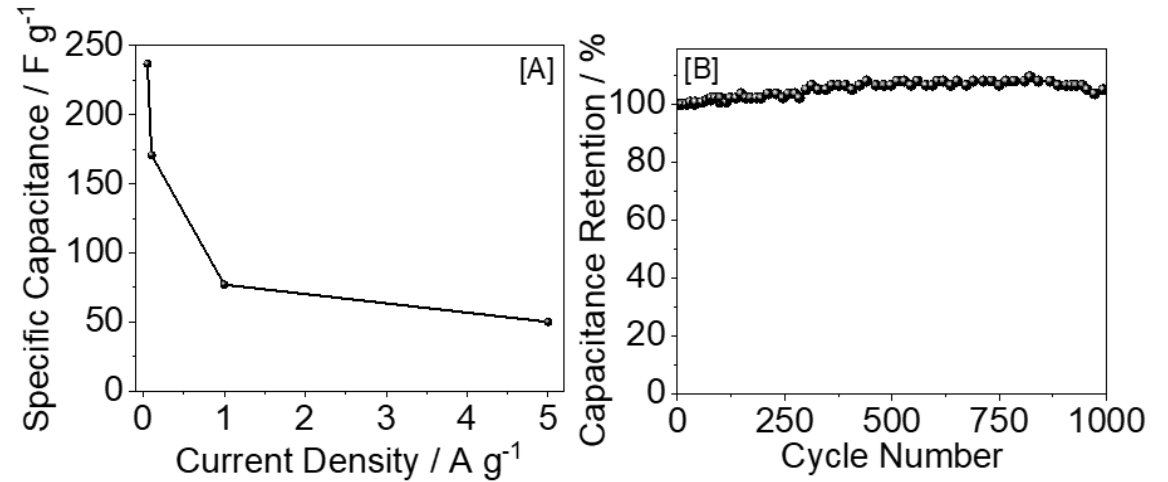
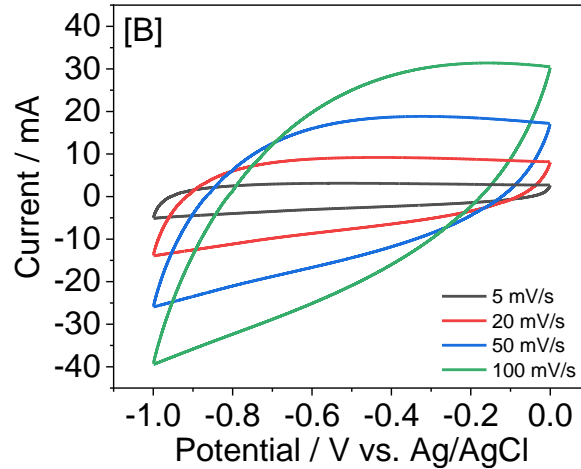
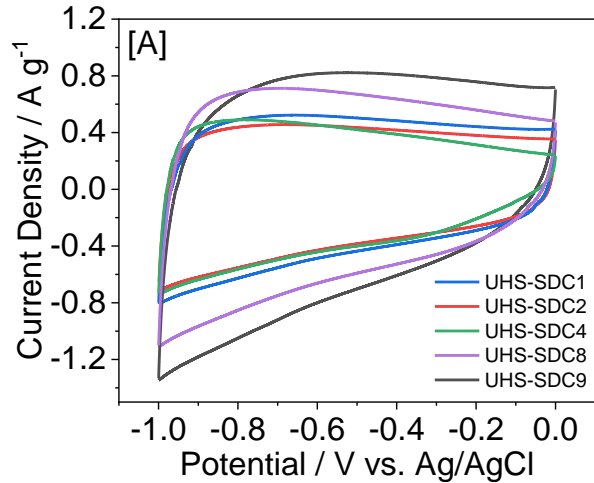
Approach-2 Preparation of Carbon Nanofibrous Felt



A. Simultaneous electrospinning and electro spraying, **B.** PAN/biochar precursor membrane, **C.** Stabilized membrane, **D.** Carbon nanofibrous felt.



Graphitization of biochar to biocarbon



Optimal processing conditions for graphitization

- Temperature: 850 °C
- Ramp rate: 5 °C min⁻¹
- Duration: 3 h
- Atmosphere: Argon (ultra high purity)

At optimal processing conditions, non-catalytic HTL of UHS derived biochar was processed to battery grade biocarbon and yielded a specific capacitance value of **242 F/g**.

Electrochemical performance compares most closely with corn stover derived biocarbon (246 F g⁻¹) Jin et al. (2014).

Shell et al., *Bioresource Tech. Reports* (2021); Jin et al., *J of Analytical and Applied Pyrolysis* (2014)

Summary

Overall: The project is in good health meeting all the milestone metrics at the laboratory scale. Corn stover preprocessing at a pilot scale yielded the desired quality. The project activities are on the verge of transition to a 1 tpd pilot scale after configuring the processing plant and setting-up the equipment, which will then follow TEA/LCA with the participation from INL.

1-Management: Task leadership involved planning, prioritizing, coordinating, and reviewing progress via bi-weekly meetings, and documenting and submitting technical and financial reports. Prompt communications, revisiting action plans and executing actions were key components.

2-Approach: Proposed integrated technology approach was validated with corn stover feedstock and experimental conditions were optimized at the lab scale for subsequent pilot plant trials.

3-Impact: Positively impacting BETO's mission of high value products revenue from waste streams, reduction in GHGs, partnerships with industries/universities/national labs, South Dakota bioprocessing pilot scale facility initiative, supports for the students/post-doc/research personnel, outreach and educational activities, and publications/presentations.

4-Progress and Outcomes: Pilot scale preprocessing and laboratory scale trials were found to be successful meeting target metrics pertaining to key milestones.

Yields: Char 42%, heavy bio-oil (HBO) 20%, lactic acid >22% and phenol >10%. Quality: biochar (specific surface area $\sim 1300 \text{ m}^2/\text{g}$), biocarbon specific capacitance 242 F g^{-1} and carbon nanofiber felt (up to 40 wt% biochar loading) and sponge (>50 wt% biochar loading) specific capacitance 225 F g^{-1} .

Response to FY-2019 Peer-Review Comments

Criteria 1: Approach

Weakness: Using the alkaline pretreatment is not standard pretreatment and no information was presented as to why this approach was taken, the concentration used, and any specific challenges to this approach.

Response: The basis of using alkaline pretreatment and the selected concentration was based on our optimized results published in "Biomass and Bioenergy 35 (2011) 956-968". The main objective of alkali addition was to study the effect of maintaining the pH of liquid hydrolysate near neutral (5-6) by conducting alkali salt (K_2CO_3) assisted hydrothermal pretreatment. The purpose was to retain hemicellulose, fractionate lignin, and minimize the loss of cellulose in liquid stream. Moreover, the addition of a small amount of K_2CO_3 increased the glucan digestibility.

Criteria 2: Relevance

Weakness: Unrealistic TEA. Poor scalability.

Response: In terms of preprocessing the chosen feedstock, corn stover has been extensively studied and made a priority with BETO's Feedstock-Conversion Interface Consortium (FCIC). Given recent advances in preprocessing technology and process intensification, the cost has been reduced and unit operations have been minimized to provide a uniform feedstock for downstream processing. Recent advances such as mechanical separation to remove harmful inorganic constituents and high-moisture densification for upcoming pilot scale trials will be applied as necessary to reduce chemical variability in the feedstock and meet process economics. A full TEA will be carried out during pilot scale trials to simulate industrially relevant conditions.

Quad Chart Overview

Timeline

- Project start date: 07/01/2018
- Project end date: 01/14/2022

	FY18	FY19	FY20	FY21	Active Project
DOE Funding	\$6,424.93	\$219,998.45	\$472,216.59	\$117,243.56	\$815,883.53
Cost Share	-----	\$28,737.89	\$53,007.83	\$14,028.22	\$95,773.94

Project Partners

- Sergio Hernandez, Idaho National Laboratory (INL)
- Ram Gupta, Virginia Commonwealth University (VCU)
- Sandeep Kumar, Old Dominion University (ODU)
- Hao Fong, South Dakota School of Mines & Technology (SDSMT)
- Southwest Research Institute (SwRI)
- NEI Corporation; Nanopareil LLC

Project Goal

- ❖ Demonstrate production of high value products (biocarbon, carbon nanofibers, lactic acid/polylactide, and phenol) from waste streams, generated during conventional biochemical processing at a pilot scale level with 1 tpd throughput.

End of %Project Milestone
70%

Barriers addressed

- ❖ Ct-J: Identification and Evaluation of Potential Bioproducts,
- ❖ Ct-K: Developing Methods for Bioproduct Production,
- ❖ ADO-A: Process Integration

Funding Mechanism

Specify lab call topic and year, if applicable.

Publications

1. Shell, Katelyn M., Dylan D. Rodene, Vinod Amar, Anuj Thakkar, Bharathkiran Maddipudi, Sandeep Kumar, Rajesh Shende, and Ram B. Gupta. "Supercapacitor Performance of Corn Stover-derived Biocarbon Produced from the Solid Co-products of a Hydrothermal Liquefaction Process." *Bioresource Technology Reports* (2021): 100625.
2. Thakkar, Anuj, Katelyn M. Shell, Martino Bertosin, Dylan D. Rodene, Vinod Amar, Alberto Bertucco, Ram B. Gupta, Rajesh Shende, and Sandeep Kumar. "Production of levulinic acid and biocarbon electrode material from corn stover through an integrated biorefinery process." *Fuel Processing Technology* (2020): 106644.
3. Amar, Vinod S., Joseph D. Houck, and Rajesh V. Shende. "Catalytic HTL-derived biochar and sol-gel synthesized (Mn, Ti)-oxides for asymmetric supercapacitors." *International Journal of Energy Research* 44, no. 15 (2020): 12546-12558.
4. Houck, Joseph D., Vinod S. Amar, and Rajesh V. Shende. "Sol-gel derived mixed phase (Mn, Ti)-oxides/graphene nanoplatelets for hybrid supercapacitors." *International Journal of Energy Research* 44(15), (2020): 12474-12484.
5. Xu, Tao, Xianfu Li, Zhipeng Liang, Vinod S. Amar, Runzhou Huang, Rajesh V. Shende, and Hao Fong. "Carbon Nanofibrous Sponge Made from Hydrothermally Generated Biochar and Electrospun Polymer Nanofibers." *Advanced Fiber Materials* (2020): 1-11.
6. Vinod Amar, Joseph Houck, Bharathkiran Maddipudi, Anuj Thakkar, Shell, Katelyn M, Sergio Hernandez, Sandeep Kumar, Ram B. Gupta, and Rajesh Shende. HTL Processing of UHS for hydro char and its use for asymmetric supercapacitors with (Mn, Ti)-oxide electrode. *Renewable Energy Journal* (under review)
7. Xianfu Li, Tao Xu, Zhipeng Liang, Vinod S. Amar, Runzhou Huang, Bharath K. Maddipudi, Rajesh V. Shende, Hao Fong. Simultaneous electrospinning and electrospaying for the preparation of precursor membrane containing hydrothermally generated biochar particles to make the value-added product of carbon nanofibrous felt. *Polymers* (under review)

Presentations

1. Vinod S. Amar, Bharat Maddipudi, Anuj Thakkar, Katelyn Shell, Dylan Rodene, Tylor Westover, Sandeep Kumar, Ram B. Gupta and Rajesh Shende, Base Catalyzed Aqueous Phase Oxidation of HTL Derived Biocrude for C1-C3 Carboxylic Acids, Virtual AIChE Annual Meeting, Nov 16 – Nov 20, 2020.
2. Vinod S. Amar, Bharat Maddipudi, Anuj Thakkar, Katelyn Shell, Dylan Rodene, Tylor Westover, Sandeep Kumar, Ram B. Gupta and Rajesh Shende, Hydrothermal Liquefaction of Unhydrolyzed Solids for Fuels and Value-Added Products, Virtual AIChE Annual Meeting, Nov 16 – Nov 20, 2020.
3. Shell, Katelyn M., Dylan D. Rodene, Vinod Amar, Anuj Thakkar, Bharathkiran Maddipudi, Sandeep Kumar, Rajesh Shende, and Ram B. Gupta, Corn Stover derived biocarbon from hydrothermal liquefaction for supercapacitor applications, Virtual AIChE Annual Meeting, Nov 16 – Nov 20, 2020.
4. Vinod S. Amar, Bharat Maddipudi, Anuj Thakkar, Katelyn Shell, Dylan Rodene, Tylor Westover, Sandeep Kumar, Ram B. Gupta and Rajesh Shende, Production of Value Added Co-Products from the Hydrothermal Liquefaction of Unhydrolyzed Solids, AIChE Annual Meeting, Nov 10 – Nov 15, 2019, FI.
5. Vinod S. Amar, Anuj Thakkar, Bharat Maddipudi, Sandeep Kumar and Rajesh Shende, Subcritical aqueous phase oxidation of the waste generated from alkaline pretreatment of lignocellulosic biomass, AIChE Annual Meeting, Nov 10 – Nov 15, 2019, FI.
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7. Vinod S. Amar, Joseph Houck and Rajesh Shende, HTL derived biochar as electrode material for supercapacitor, AIChE Annual Meeting, Nov 10 – Nov 15, 2019, FI.

Management Approach



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- ❖ **Task leadership: plan, prioritize, coordinate, review progress**
 - Bi-weekly team coordination meetings – PI & CO-PI, Students & Post-docs
 - Bi-weekly team coordination meetings with DOE personnel (as needed)
 - Quarterly DOE project progress reports and financial summary
 - Prompt communication among team members
 - Revisiting action plan and executing actions

- ❖ **Create and follow approved management plans**
 - Milestones (quarterly) and deliverables
 - Performance metrics and milestones

- ❖ **Responsibilities**
 - Corn stover preprocessing and pilot scale alkaline pretreatment and enzymatic hydrolysis: Sergio Hernandez
 - Alkaline pretreatment and enzymatic hydrolysis (lab scale): Sandeep Kumar
 - Hydrothermal liquefaction and wet oxidation (lab and pilot): Rajesh Shende
 - Conversion of char into biocarbon (lab): Ram Gupta, (pilot) Mark Feng
 - Conversion of char into carbon nanofibers (0.5-1 kg/day): Hao Fong
 - Dissemination of results (publications, presentation): All partners

Preprocessing: Biomass Feedstock National User Facility

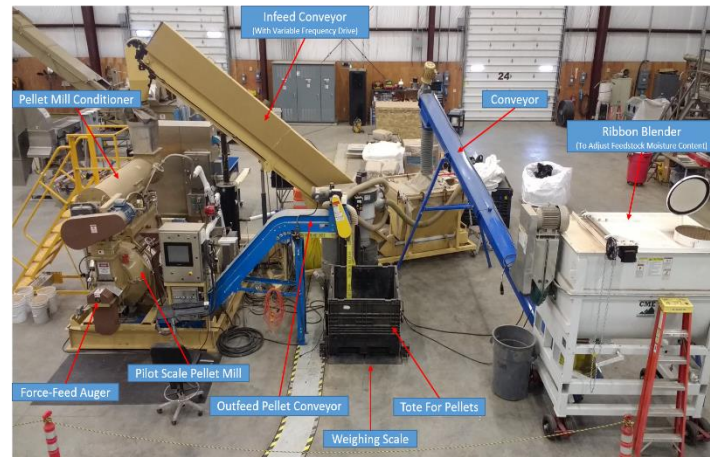
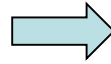


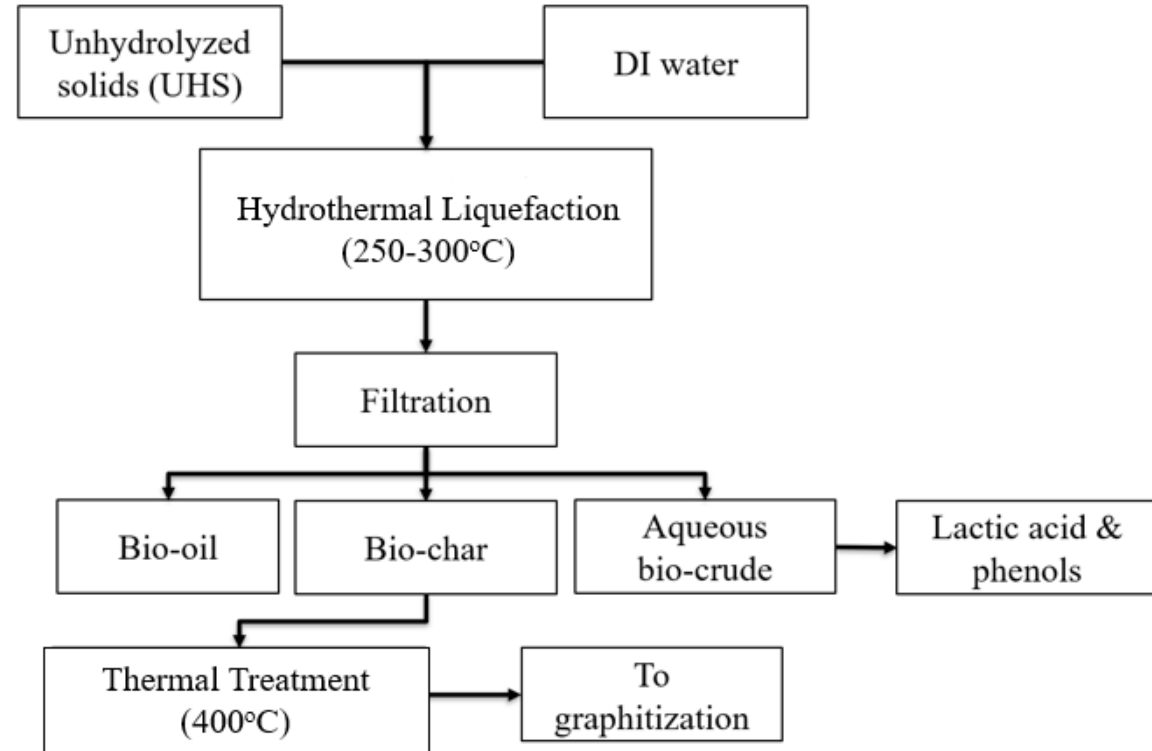
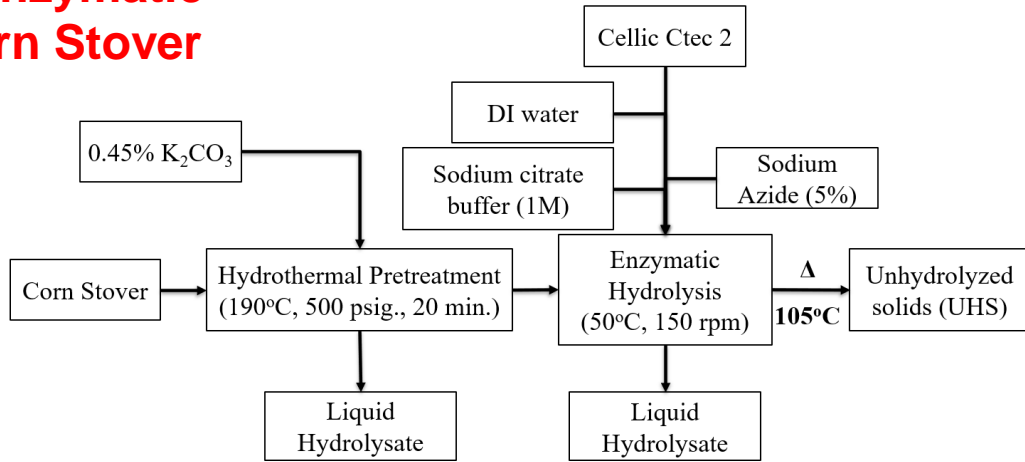
Table 3. Breakdown of modeled, estimated cost per ton of each unit operation for various preprocessing pathways using combined mechanical and chemical preprocessing [1,2,3].

Feedstock Pathways	Corn Stover Bale Preprocessing
Rotary Dryer (optional)	\$12.50
Conveyor	\$0.70
Mechanical Separation (optional sieving)	\$1.00
Air Classifier (optional)	\$2.81
Chemical Pretreatment and Drying	\$29.15
Size Reduction	\$17.21
Pelletization	\$7.68

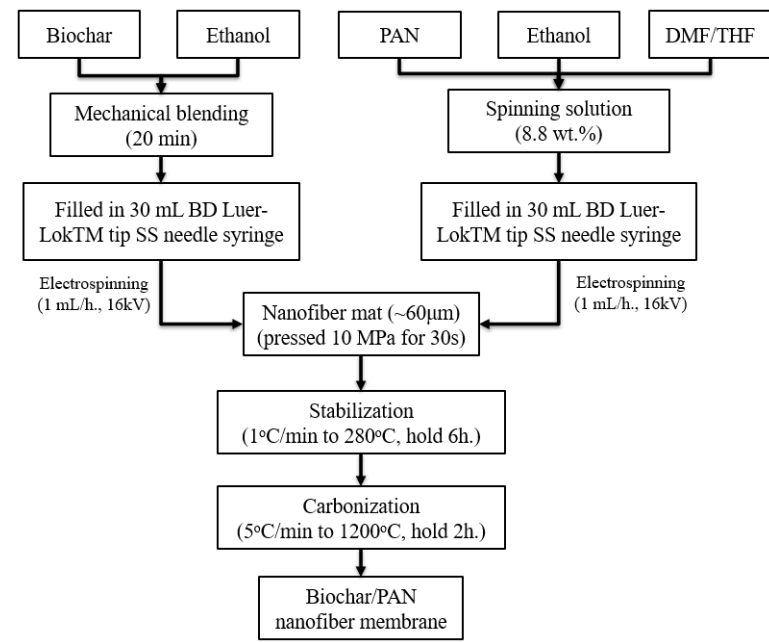
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2. Hu, H., Westover, T.L., Cherry, R. et al. Process Simulation and Cost Analysis for Removing Inorganics from Wood Chips Using Combined Mechanical and Chemical Preprocessing. *Bioenergy Research* 10, 237–247 (2017).
3. Jaya Shankar Tumuluru, Kara G Cafferty, Kevin L Kenney. 2014. Techno-economic Analysis of Conventional, High Moisture Pelletization and Briquetting Process. ASABE Annual meeting, Paper #141911360, Montreal, Quebec Canada July 13 – July 16, 2014.

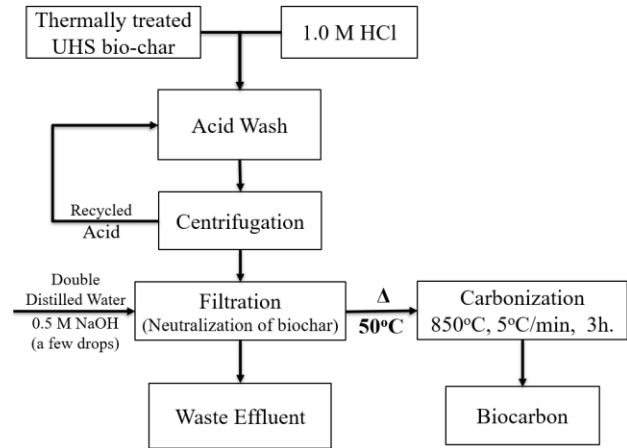
Pretreatment & Enzymatic Hydrolysis of Corn Stover



Hydrothermal Liquefaction of Unhydrolyzed Solids (UHS)



Electrospinning of biochar/PAN to Nanofiber membrane



Graphitization of biochar to biocarbon